A Literature Investigation about Electrospinning and Nanofibers: Historical Trends, Current Status and Future Challenges

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Abstract: The development of new fibrilar materials based on electrospinning (ES) technique has a notable history of nearly four centuries of discoveries and results. The eletrospinning manufacturing is one of the most widely reported methods for nanofiber (NF) manufacturing, providing security, high quality and productivity. In spite of the first patent about electrospinning has been applied in April 5th, 1900 by John Francis Cooley, a historical perspective (since 1600s) about this amazing discovery represents an important step for future applications. Nanofibers have been considered one of the top interesting fundamental study objects for academicians, and greatest intriguing business materials for modern industry. As a consequence, lucrative organizations and companies have explored the relevance of nanofibers. In this paper, the quantity of published manuscripts and patent inventions is presented and the correlation of research activities to the production of new electrospinning materials is shown. China and the United States have been leading in electrospinning and nanofibers development. The company triumph is mostly dependent on applications improvement relevant for broader business society. A dramatic rise of interest in nanofibers produced by electrospinning technique has been confirmed due to the publication data, author's affiliation, keywords, and essential characterization procedures. Is has been shown that the number of publications on electrospinning and nanofibers researches from academic institutions is higher than industrial laboratories. More than 1,891 patents using the term "*electrospinning*" and 2,960 with the term "nanofibers" according to the European Patent Office at title or abstract have been filed around the world up to 2013. These numbers just continue to increase along with worldwide ES-related sales. Curiously, for the same period 11,973 electrospinning documents and 18,679 nanofibers-related (mainly manuscripts) were published considering the Scopus database with the same terms in the title, abstract or using keywords. Thus, statistically, there are more published manuscripts worldwide than patents for both keywords.

Keywords: Electrospinning, history, nanofibers, nanotechnology, patent, technology.

1. INTRODUCTION

The nanofiber (NF) production by electrospinning (ES) technique has a long history of almost four centuries, but only in the last decades this process has achieved widespread popularity in academia as well as industries. It is a method for manufacturing continuous nano-scale fibers. However, during these centuries, the understanding of electrospinning was far from complete, almost empirical. The first modern work describing the performance of fluid droplets at the extremity of metal capillaries on electrospun fibers was reported by the Czech-American physicist John Zeleny (1872-1951) a century ago [1].

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According to Tucker *et al*. [2], the beginning of this history dates back to the XVII century, when the first record about electrostatic attraction between liquids was noted by the English physician, physicist and natural philosopher William Gilbert (1544-1603). At his work "*De Magnete*" (1600), Book II, Chapter II: "On Magnetic Coition; and, First, of the Attraction Exerted by Amber, or more Properly the Attachment of Bodies to Amber", he prepared an experiment and observed when a nearly spherical water drop on a dry surface deformed into a cone shape when near a piece of amber charged electrically was held at a proper distance above it [3]. As noted by Tucker *et al*. [2], this could be considered the first record of the deformation of a liquid droplet into what would become known as the Taylor cone. The German-Swiss chemist Christian Friedrich Schönbein (1799-1868) prepared for the first time in 1846 a high content of nitrated cellulose. In 1882 [4] the English physicist Lord Rayleigh (John William Strutt, 1842-1919) analyzed the instability

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condition in liquid droplets that were electrically charged, and noted that when the surface tension is equilibrated by the electrostatic force the liquid is ejected in tiny jets. The British physicist Charles Vernon Boys (1855-1944) published a manuscript in 1887 about the nanofiber development and production. The American inventor John Francis Cooley (1861-1903) published in 1900 the first modern electrospinning patent [5] (*G.B. patent* 6,385: Improved Methods of and Apparatus for Electrically Separating the Relatively Volatile Liquid Component from the Component of Relatively Fixed Substances of Composite Fluids, (Fig. **1**, *left*). His studies started to model mathematically the performance of fluids under electrostatic forces. Cooley was followed by William James Morton (1845-1920), that also filed a patent in 1902 (*U.S.* patent 705, 691: Method of Dispersing Fluids [6]). In 1934-1944 period, Anton Formhals (1877-1956) took out at least 22 patents on electrospinning, the first shown in (Fig. **1**, *right*) [7] (*U.S.* Patent 1,975,504: Process and Apparatus for Preparing Artificial Threads, 1934). In 1938, Nikolai Albertowich Fuchs (1895-1982), Nathalie D. Rozenblum (who was unfortunately executed during the Stalin period) and Igor Vasil'evich Petryanov-Sokolov (1907-1996) produced electrospun fibers, thus promoting the first commercial application of filters using NFs. In 1964-1969 period, *Sir* Geoffrey Ingram Taylor (1886-1975) introduced the first physical concept about electrospinning by mathematical modeling the pattern of the (Taylor) cone done by the fluid droplet under the action of an electric field. Since 1990s many institutions as well as research groups (noticeably that of Darrell H. Reneker, who popularized ES) demonstrated and applied electrospun nanofibers. In the period observed by this research, experts like S. Ramakrishna (Singapore), H. Y. Kim (South Korea), P. Supaphol (Thailand), A. Greiner (Germany), S. I. Stupp (US) and C. Wang (China) made significant and prolific contributions that revitalized the electrospinning / nanofiber technologies to a new time of progressive and novel functional materials. These researches moved toward the development of leading composites from many polymers for new nanotechnological applications, which promoted an exponential increase in the number of publications, beneficial to industry community [8].

Our understanding about electrospinning process has been updated in the virtually four hundred years that have followed this revolutionary period, but only at the end of XX century the keywords "electrospinning" and "nanofibers" were more used by scientists and researchers. In fact, the term "electrospinning", resulting from "electrostatic spinning", has been used only in recent times. For this reason, the analysis will consider more the 1990s up to 2013. In addition, nanofibers are related to nanostructured materials; their dimensions (particularly diameter) change from quite a few tens up to hundreds of nanometers. Due to their morphology, nanofibers have particular properties, which provide potential business in a lot of areas, as battery separators, filters, medical textiles, etc, allowing its progressive use on reliable industrial technologies by different industries in order to manufacture NFs [9].

Due to its potential production of tiny fibers with narrow or even no pores, large surface area-to-volume ratio (this ratio can be as large as 10^3 times when compared with a microfiber), low basis weight and flexibility [10], NFs have been considered as a potential candidate for unique functions in high-tech industrial companies.

Electrospun nanofibers present promising applications, as for repairing or bone replacement, cartilage, muscle and other whole tissues with a grouping of engineered biomaterials and other biological nanosystems. Science investigators discovered the relevance of nanofibers as a 3-D scaffold support for stem-cell tissue engineering as well as bone tissue [11].

Nanofiber inclusions allow a new production of highly developed air filter media that increases filtration efficiency, but with lower pressure drop. Further properties targeted for enhancement by researchers incorporate tensile strength, conductive and transport properties using NFs [12]. Biomedical applications are improved if considered the incorporation of nanoparticles in electrospun fibers, which contributes with development of artificial skin with additional protection against UVA/UVB radiation [13].

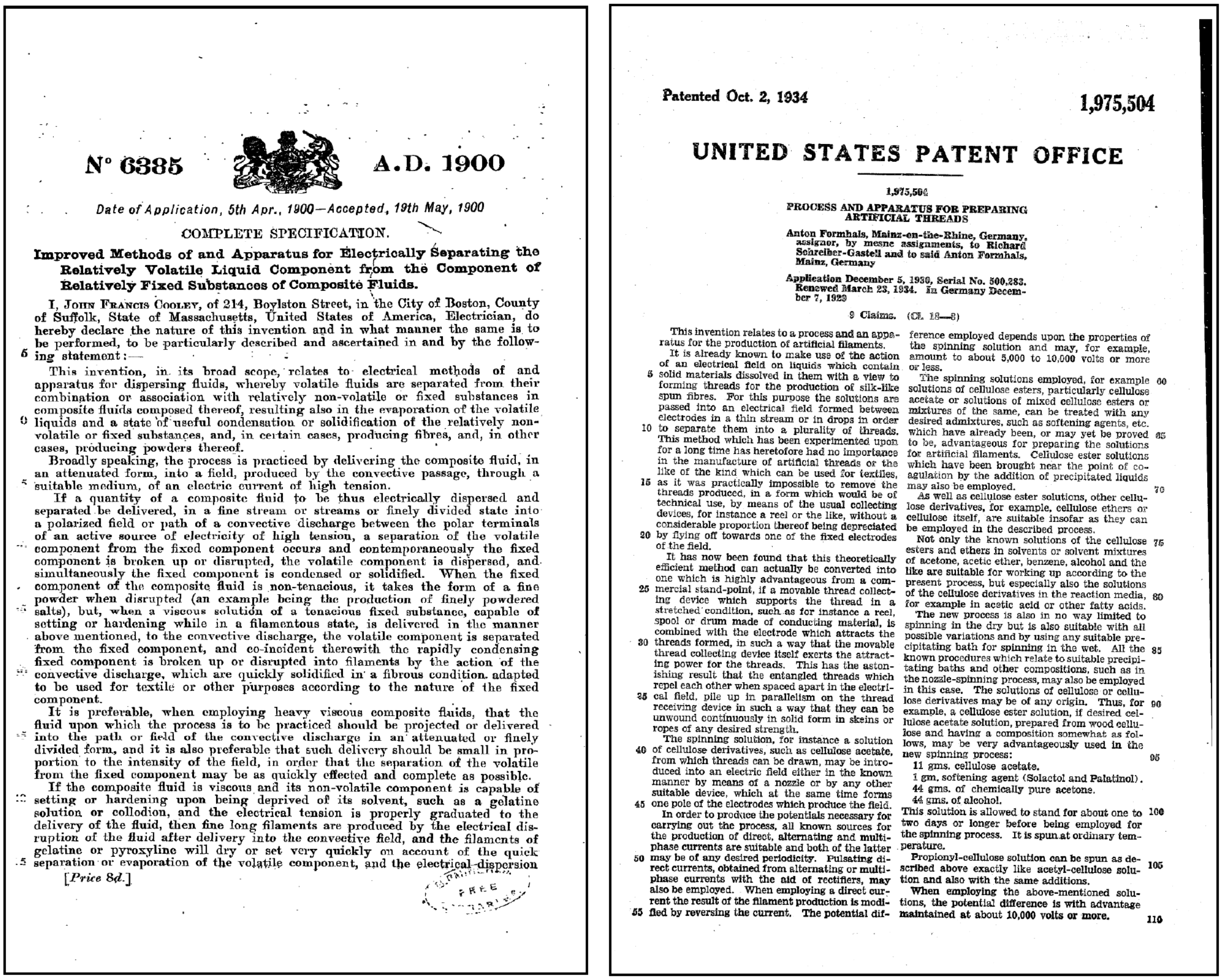
Our goal is to present an overview of the historical tendencies and present situation of ES and NFs studies. We hope this paper can be used as an exploratory revision to be used during discussion about future guidelines for electrospinning and nanofibers researches by describing the development of electrospun discoveries based on the literature.

2. METHODOLOGY

In this work, we have considered the number of published manuscripts catalogued in the "Life Sciences" (which comprises 4,300 journal titles), "Health Sciences" (6,800 titles), "Physical Sciences" (7,200 titles) and "Social Sciences & Humanities" (5,300 titles) libraries of the Scopus bibliographic database from Elsevier due to wide application range of our research. We searched for papers with the words "electrospinning," "nanofiber" in the *title*, *abstract* or *keywords* of the articles. With this chosen search strategy, we excluded many other electrospinning and nanofibers-related articles. However, this approach provided a broader dataset and consequently, sufficient data for statistical analysis.

The total number of electrospinning published manuscripts registered at Scopus was 11,973 based on the keyword ("electrospinning") appearing in the article title, keyword list, or abstract, for all document types, including letters, *errata*, conference proceedings and technical notes between 1990 up to 2013. The same procedure for nanofibers gave 18,679 documents. To further simplify our dataset we restricted the search to journal articles only for the same period. Our search returned 9,333 electrospinning-related manuscripts from the Scopus database, 13,356 documents related to nanofiber studies. A similar search carried out on the Web of Science (Thomson Reuters Scientific) returned a similar result, *viz*., around 11,982 manuscripts when searching for the terms "*electrospinning*" at title or topic, and 23,637 for "*nanofibers*" keywords. The articles obtained through this approach were grouped according to the research field, including journal title, publication date, affiliation, country of origin, and type studied.

It was also executed a similar research of the patent literature by means of the European Patent Office database. This search considered patents awarded between 1990 and



N° 6385 A.D. 1900

Date of Application, 5th Apr., 1900—Accepted, 19th May, 1900

COMPLETE SPECIFICATION.

Improved Methods of and Apparatus for Electrically Separating the Relatively Volatile Liquid Component from the Component of Relatively Fixed Substances of Composite Fluids.

I, JOHN FRANCIS COOLEY, of 214, Boylston Street, in the City of Boston, County of Suffolk, State of Massachusetts, United States of America, Electrician, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention, in its broad scope, relates to electrical methods of and apparatus for dispersing fluids, whereby volatile fluids are separated from their combination or association with relatively non-volatile or fixed substances in composite fluids composed thereof, resulting also in the evaporation of the volatile liquids and a state of useful condensation or solidification of the relatively non-volatile or fixed substances, and, in certain cases, producing fibres, and, in other cases, producing powders thereof.

Broadly speaking, the process is practiced by delivering the composite fluid, in an attenuated form, into a field, produced by the convective passage, through a suitable medium, of an electric current of high tension.

If a quantity of a composite fluid to be thus electrically dispersed and separated be delivered, in a fine stream or streams or finely divided state into a polarized field or path of a convective discharge between the polar terminals of an active source of electricity of high tension, a separation of the volatile component from the fixed component occurs and contemporaneously the fixed component is broken up or disrupted, the volatile component is dispersed, and simultaneously the fixed component is condensed or solidified. When the fixed component of the composite fluid is non-tenacious, it takes the form of a fine powder when disrupted (an example being the production of finely powdered salts), but, when a viscous solution of a tenacious fixed substance, capable of setting or hardening while in a filamentous state, is delivered in the manner above mentioned, to the convective discharge, the volatile component is separated from the fixed component, and co-incident therewith the rapidly condensing fixed component is broken up or disrupted into filaments by the action of the convective discharge, which are quickly solidified in a fibrous condition adapted to be used for textile or other purposes according to the nature of the fixed component.

It is preferable, when employing heavy viscous composite fluids, that the fluid upon which the process is to be practiced should be projected or delivered into the path or field of the convective discharge in an attenuated or finely divided form, and it is also preferable that such delivery should be small in proportion to the intensity of the field, in order that the separation of the volatile from the fixed component may be as quickly effected and complete as possible.

If the composite fluid is viscous and its non-volatile component is capable of setting or hardening upon being deprived of its solvent, such as a gelatine solution or collodion, and the electrical tension is properly graduated to the delivery of the fluid, then fine long filaments are produced by the electrical disruption of the fluid after delivery into the convective field, and the filaments of gelatine or pyroxyline will dry or set very quickly on account of the quick separation or evaporation of the volatile component, and the electrical dispersion

[*Price 8d.*]

Patented Oct. 2, 1934 1,975,504

UNITED STATES PATENT OFFICE

1,975,504

PROCESS AND APPARATUS FOR PREPARING ARTIFICIAL THREADS

Anton Formhals, Mainz-on-the-Rhine, Germany, assignor, by mesne assignments, to Richard Schreiber-Gastell and to said Anton Formhals, Mainz, Germany

Application December 5, 1930, Serial No. 500,283. Renewed March 23, 1934. In Germany December 7, 1929

9 Claims. (Cl. 18—8)

This invention relates to a process and an apparatus for the production of artificial filaments.

It is already known to make use of the action of an electrical field on liquids which contain solid materials dissolved in them with a view to forming threads for the production of silk-like spun fibres. For this purpose the solutions are passed into an electrical field formed between electrodes in a thin stream or in drops in order to separate them into a plurality of threads. This method which has been experimented upon for a long time has heretofore had no importance in the manufacture of artificial threads or the like of the kind which can be used for textiles, as it was practically impossible to remove the threads produced, in a form which would be of technical use, by means of the usual collecting devices, for instance a reel or the like, without a considerable proportion thereof being depreciated by flying off towards one of the fixed electrodes of the field.

It has now been found that this theoretically efficient method can actually be converted into one which is highly advantageous from a commercial stand-point, if a movable thread collecting device which supports the thread in a stretched condition, such as for instance a reel, spool or drum made of conducting material, is combined with the electrode which attracts the threads formed, in such a way that the movable thread collecting device itself exerts the attracting power for the threads. This has the astonishing result that the entangled threads which repel each other when spaced apart in the electrical field, pile up in parallelism on the thread receiving device in such a way that they can be unwound continuously in solid form in skeins or ropes of any desired strength.

The spinning solution, for instance a solution of cellulose derivatives, such as cellulose acetate, from which threads can be drawn, may be introduced into an electric field either in the known manner by means of a nozzle or by any other suitable device, which at the same time forms one pole of the electrodes which produce the field.

In order to produce the potentials necessary for carrying out the process, all known sources for the production of direct, alternating and multiphase currents are suitable and both of the latter may be of any desired periodicity. Pulsating direct currents, obtained from alternating or multiphase currents with the aid of rectifiers, may also be employed. When employing a direct current the result of the filament production is modified by reversing the current. The potential difference employed depends upon the properties of the spinning solution and may, for example, amount to about 5,000 to 10,000 volts or more or less.

The spinning solutions employed, for example solutions of cellulose esters, particularly cellulose acetate or solutions of mixed cellulose esters or mixtures of the same, can be treated with any desired admixtures, such as softening agents, etc. which have already been, or may yet be proved to be, advantageous for preparing the solutions for artificial filaments. Cellulose ester solutions which have been brought near the point of coagulation by the addition of precipitated liquids may also be employed.

As well as cellulose ester solutions, other cellulose derivatives, for example, cellulose ethers or cellulose itself, are suitable insofar as they can be employed in the described process.

Not only the known solutions of the cellulose esters and ethers in solvents or solvent mixtures of acetone, acetic ether, benzene, alcohol and the like are suitable for working up according to the present process, but especially also the solutions of the cellulose derivatives in the reaction media, for example in acetic acid or other fatty acids.

The new process is also in no way limited to spinning in the dry but is also suitable with all possible variations and by using any suitable precipitating bath for spinning in the wet. All the known procedures which relate to suitable precipitating baths and other compositions, such as in the nozzle-spinning process, may also be employed in this case. The solutions of cellulose or cellulose derivatives may be of any origin. Thus, for example, a cellulose ester solution, if desired cellulose acetate solution, prepared from wood cellulose and having a composition somewhat as follows, may be very advantageously used in the new spinning process:

11 gms. cellulose acetate.
1 gm. softening agent (Solactol and Palatinol).
44 gms. of chemically pure acetone.
44 gms. of alcohol.

This solution is allowed to stand for about one to two days or longer before being employed for the spinning process. It is spun at ordinary temperature.

Propionyl-cellulose solution can be spun as described above exactly like acetyl-cellulose solution and also with the same additions.

When employing the above-mentioned solutions, the potential difference is with advantage maintained at about 10,000 volts or more.

Fig. (1). *Left*: the first page of *United Kingdom* patent *G.B.* 6,385 (www.ipo.gov.uk) applied by Cooley on April 5th, 1900 [5]. *Right*: the first page of *United States* patent 1,975,504 (www.uspto.gov) applied by Formhals on October 2nd, 1934 (filed in December 5th, 1930) [7].

2013 with the keywords in the title and title or abstract as was performed in the Scopus research. The result returned approximately 1,891 electrospinning as well as 2,960 nanofiber patents, both issued around the world. These patents founded were classified according to issue date and inventor.

3. RESULTS & DISCUSSION

Fig. (**2 a, b**) presents a comparison of the quantity of electrospinning-related documents and patents published and granted by year, as found through the Scopus database. Here we considered the following search strategies: the ES keywords were founded in the article title, abstract or keywords list (11,973 documents); only in the abstract (9,333 documents) and just in the title (3,489 documents), see (Fig. **2 a**); or keywords appearing in the patent in a similar way, according to (Fig. **2 b**). Fig. (**2 a**) presents the quantity of publications on electrospinning based research works exponentially increased in recent years, which is correlated with the observations made by Huang *et al.* [9]. According to (Fig. **2 b**) there is an increasing on filled patents, but not in the same behavior as obtained in different publications. In fact, the number of patents awarded and concerning ES process had been rising gradually since 1990s and but still did not reach a higher number per year than those of printed manuscripts. This is an indication that this technique still must increase as a promising scientific knowledge among the researchers and organizations (as institutes and industries). About 711 electrospinning-related patents have been granted around the world in the past 25 years.

Regarding electrospinning documents, 77.90 % were Articles, 15.81 % were Conference Papers and only 3.59 % were Reviews. Other reported categories included Book Chapters, Conference Reviews and Letters. Similar results, of 75.19 % Articles, 19.34 % Conference Papers and only 2.76 % Reviews were obtained considering nanofibers research documents.

If considered (Figs. **2 c, d**), it is possible to see that granted patents taking into account nanofibers as a topic have been progressively reported since 1990s in a higher rate when viewed in comparison with (Fig. **2 a**) but not yet comparable

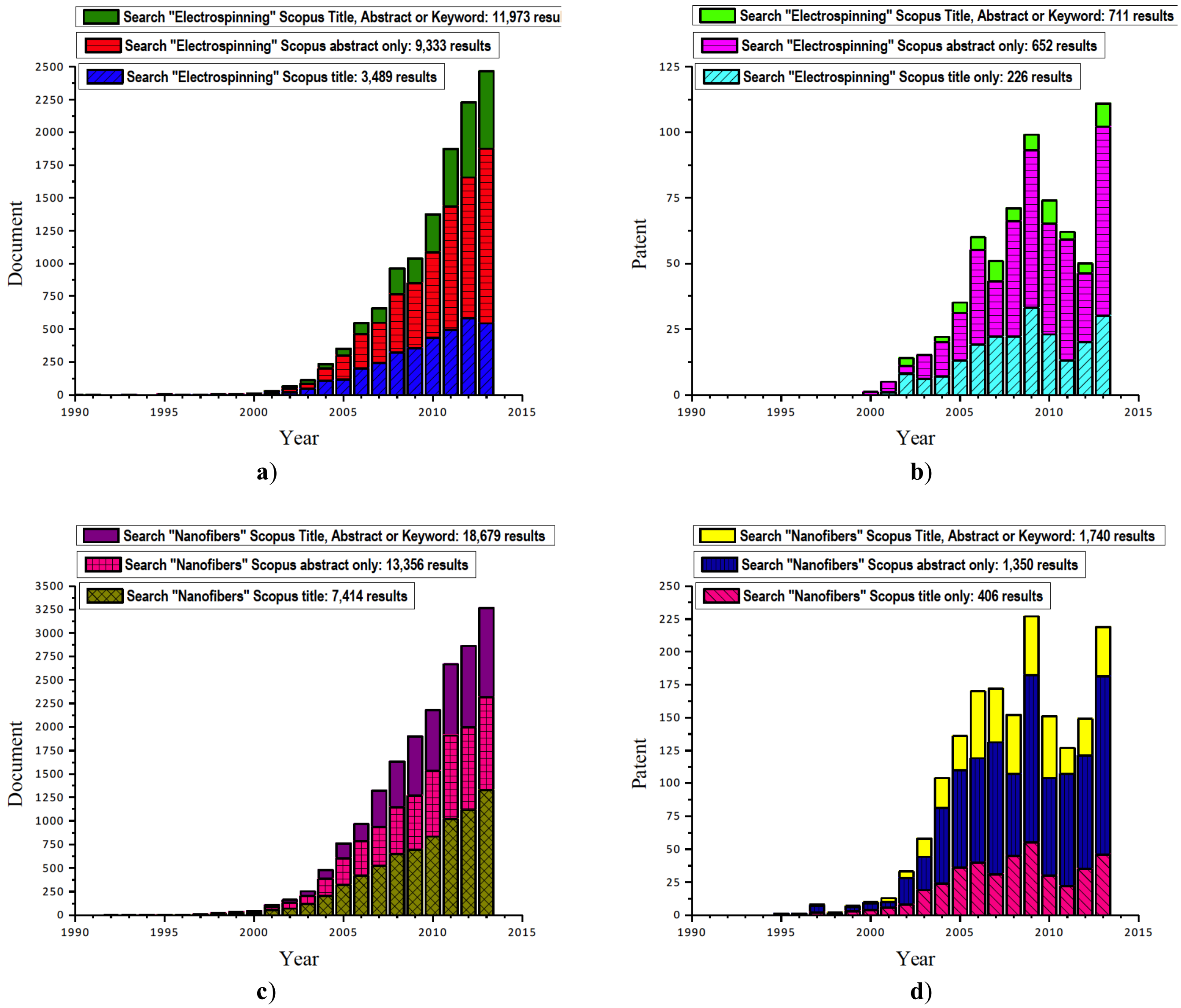


Fig. (2). (**a, b**). Publication results on “Electrospinning” documents (**a**): considering keyword in the article title, abstract or keywords (11,973 documents); only abstract (9,333 documents) and only title (3,489 documents). The same procedure on “Electrospinning” patent search (**b**): considering keyword in the article title, abstract or keywords (711 results); only abstract (652 results) and only title (226 results). (**c**, **d**). Publication results on “Nanofibers” documents (**c**): considering keyword in the article title, abstract or keywords (18,679 documents); only abstract (13,356 documents) and only title (7,414 documents). The same procedure on “Nanofibers” patent search (**d**): considering keyword in the article title, abstract or keywords (1,740 results); only abstract (1,350 results) and only title (406 results). Data from www.scopus.com.

to the number of published manuscripts. The number of published patents is also higher using nanofibers than electrospinning by a factor of two, comparing (Figs. **2 b** and **d**). A decrease on the number of patents between 2009 and 2012 was observed on Scopus database, probably due to the global financial crisis occurred in 2009.

According (Fig. **3 a**), the most productive institution in terms of patents was the Donghua University in China, leaded by Profs. Bin Ding, Limin Zhu and Jianyong Yu, among others. Asian universities, including National University of Singapore, Jilin University (China), Chonbuk National University (South Korea), and the Tsinghua University (China) were also part of the top ten institutions in a list of 160. The most productive author was Prof. Seeram Ramakrishna, from National University of Singapore, with 284 documents published in this period.

Fig. (**3 b**) shows the similar data for NFs. The top five institutions were the same, with a minor change in the first and second positions. The most productive authors were Prof. Seeram Ramakrishna, from National University of Singapore, with 268 documents published in this period, followed by Prof. Hakyong Kim with 140 documents published, from Chonbuk National University. Several Russian, European and *U.S.* universities also appear among the most overall productive institutions. It is important to note that there was none industrial research lab near the top of both lists.

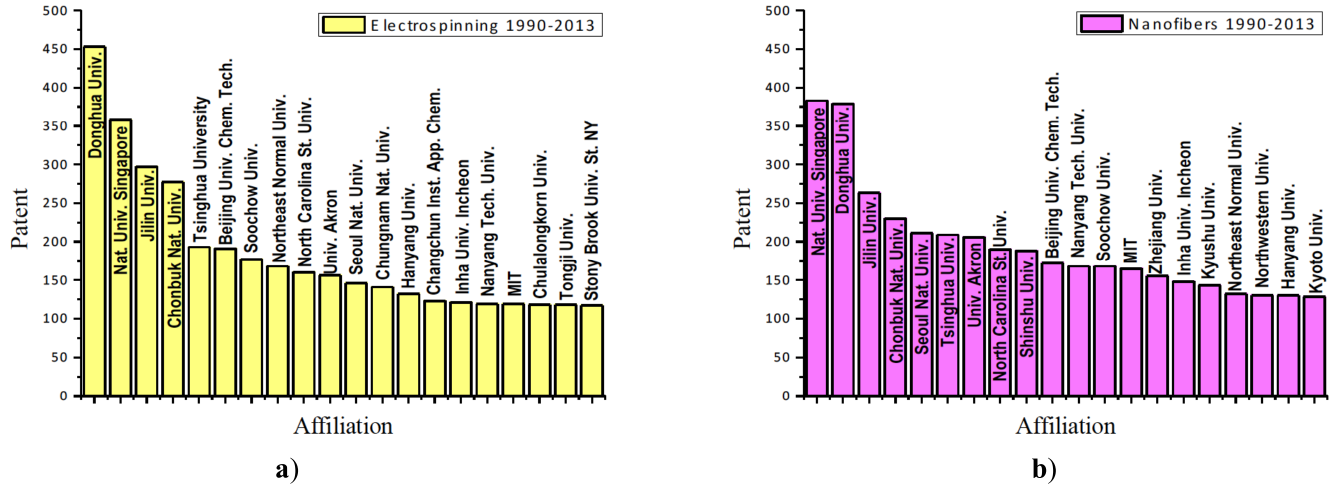


Fig. (3). (**a**) Total number of publication manuscripts in electrospinning process (1990-2013), categorized by affiliation (top 20). The Donghua University of China leads this ranking, followed by the National University of Singapore. (**b**) The same procedure of total number of publication manuscripts in nanofibers (1990-2013), categorized by affiliation (top 20), where the National University of Singapore changed position with Donghua University. In general, there is a blend of Japanese, Indian, European, Russian, Chinese and American institutions. It is pertinent to note the presence of some American universities within the 20 most productive institutions in this ranking. Data from www.scopus.com.

If we consider the number of publications on electrospinning and nanofibers-related documents by country (see Figs. **4 a**, **b**), China aggregated the highest cumulative number of overall results, followed by the United States of America, South Korea and Japan. Singapore, Germany and the United Kingdom were also ranked (Fig. **4 a**). Outside of Europe, for the same figure, India and Iran were also highly ranked.

Still on the most productive countries, (Fig. **4 a**) also presents a geographic location analysis of research scientists in the ES field. China had the highest percentage at 26.88 % of 88 countries, followed by the United States (19.73 %), South Korea (10.23 %), Japan (4.24 %) and Singapore (3.13 %). Asia contribution (taking into account only the top five institutions) is probably due to the elevated percentage of government financial support in the areas of environment and sustainable energy. China, South Korea, Japan, Singapore, India and Taiwan (11th position in this ranking) represented the top locations in Asia for nanofiber based studies and development researches, totalizing 48.5%. As a curiosity, Brazil is at the 22nd position with 102 patents, after Czech Republic, with two more patents considering electrospinning research.

A detailed number of results about the active development of "nanofiber" topic *viz*. academia (*i.e*., including universities and academic unities) focused on nanofibers based on geographical location is also presented in (Fig. **4 b**). China, *U.S*., South Korea and Japan were the overall leaders. Similarly, China reached the first position of 22.27 % of 99 countries in NFs research, followed by the United States (21.78 %), South Korea (7.77 %), Japan (7.21 %) and India (3.02 %). Thus, the United States were significant in North America, sharing more than 22% of worldwide nanofiber research activities. *U.S*. academic institutions used many types of nanofibrous composites to mainly get best energy-efficient energy conversions, water purification and energy-saving air, as well as tailored nanofibers for tissue engineering and drug delivery structures. In particular, according to (Fig. **4 b**), Japan, South Korea and Singapore were very active in exploring nanofibers mainly from electrospinning to develop the performance in energy devices *i.e*. as porous battery separators or even thin solar cell / or fuel cell electrodes.

According to these data, following (Fig. **4**), Europe had become well-known region for emergent scale up technologies for producing nanofibers, as well as using them to focus on the challenges in biomedical, nano-safety, agricultural and energy storage, with whole percentage of about 11.5 % from Germany (2.99 %), UK (2.40 %), Spain (2.02 %), France (1.70 %), Italy (1.57 %) and Sweden (1.00 %) at the top 20 for the period observed. Brazil was at the 19th position.

South Korea presented a reasonable grown and can be considered as a major significance in electrospinning and nanofiber research fields as compared with other countries. Chinese institutions and organizations rule the electrospinning and nanofiber landscapes in terms of published manuscripts, especially in energy and regenerative medicine topics, that have been increasing in recent years. Japan was also seriously growing NF research and development activities in materials science, chemistry and engineering fields (in agreement with the next results – on publication and subject areas, see below), and expanded the quantity of support of realistic funding schemes by means of the National Science Foundation, the Japan Science and Technology Agency, as well as private companies.

A perspective analysis around publishing nanofibers activity shows that around 45% NF researcher studies were from Asia, mainly China (22.27 %), South Korea (7.77 %), Japan (7.21 %) India (3.02 %), Singapore (2.36 %), and Taiwan (1.63 %), with a small contribution from other countries.

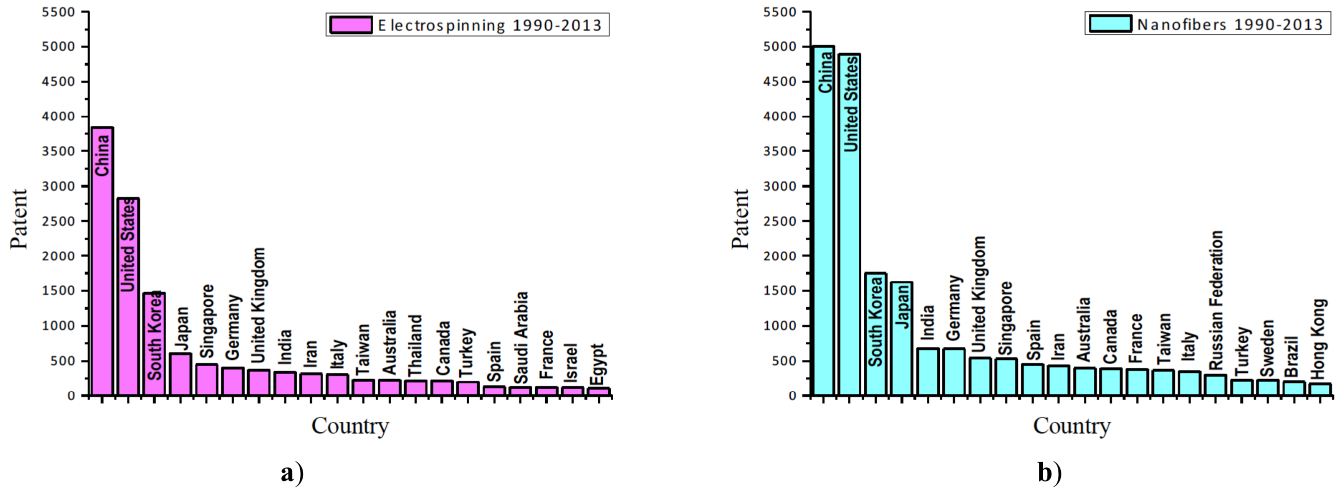


Fig. (4). Most productive20 countries in the history of electrospinning (**a**) and nanofiber (**b**) researches (1990-2013). China and the United States are the leaders overall in both analysis, followed by South Korea and Japan. Data from www.scopus.com.

The most outstanding scientific magazines and journals within the electrospinning area included *Journal of Applied Polymer Science* (4.77 %), *Advanced Materials Research* (3.73 %), *Materials Letters* (3.09 %), *Polymer* (2.92 %) and *Biomaterials* (2.41 %) are clearly the most important. Additionally, there were a number of applications and sources of publications, totalizing 11,973 manuscripts. The first journal published more than two times the quantity of electrospinning-related articles in comparison with the fifth most popular journal, as shown in (Fig. **5 a**).

From (Fig. **5 b**), if taking into account nanofibers as the topic, we observed a preference for the same two first prominent journals: *Journal of Applied Polymer Science* (3.19 %), and *Advanced Materials Research* (3.08 %). In third place appeared the period *Carbon* (2.76 %), followed by *Journal of Nanoscience and Nanotechnology* (2.52 %) and *Materials Letters* (2.29 %) as the top five. It is also important to note that there are more published works using nanofibers as a keyword, totalizing 18,679 manuscripts.

Electrospinning-related publications were also categorized by broad scientific field, such as *Materials Science* (29.35 %), followed by *Engineering* (16.86 %), *Chemistry* (15.67 %), *Chemical Engineering* (11.42 %) and *Physics* (9.98 %). The next subjects were *Biochemistry, Genetics and Molecular Biology* (6.28 %) and *Medicine* (2.71 %). Similar results were obtained in nanofibers research: *Materials Science* (28.36 %), followed by *Chemistry* (17.07 %), *Engineering* (17.06 %), *Physics* (11.88 %) and *Chemical Engineering* (11.02 %). The next subjects were *Biochemistry, Genetics and Molecular Biology* (4.47 %) and *Medicine* (2.09 %). All these results confirm that some researches done for nanofibers are related to electrospinning process. Another noteworthy trend is the absence of relevant specialized journals in such period.

Over 1,891 electrospinning patents from the European Patent Office (EPO) were granted between 1990 and 2013 (Fig. **6 a**) and 2,960 nanofiber patents for the same period (Fig. **6 b**). These results suggested that a number of innovative studies towards the development of new ES and NFs addressed to industrial challenges, and that the application markets were expanding. There was a noted decrease in the number of published patents, as observed in (Figs. **2 b**, **d**) obtained from Scopus database. At least there are two reasons: first, the number of published patents is higher at EPO than Scopus database (even considering the period 2009-2013 cited above); second, one must be aware in both cases, however, that it is a widespread industrial practice to fill numerous related patent applications in different countries considering identical invention. Therefore, the quantity of patents should be higher than the real number of single inventions, considering same authors and / or companies. Such results are also in agreement with researches done in other topics, as glassy X-ray tube patents [14] or even the industrial float glass process [15].

As shown in (Fig. **6**), considering electrospinning process and nanofibers researches, two types of patents are capable for penetrating the market fruitfully: first category is on *production technology*, *i.e.* inventions that propose cost-effective technology / accessories and growing the manufacture capacity. One well know example was that granted by Berry [16] (*U.S.* Patent 4,965,110), on the manufacture of tubular format, where it was detailed that by means of an asymmetrically inserting rotating and charged mandrel between two charged plates, it was possible to produce oriented tiny fibers by electrospun in opposition to the longitudinal axis of the tubular system. Innovations in this way embrace the promise of decreasing the capital investment and running costs for making NFs of higher qualities. Elmarco, the industrial scale equipment producer in Europe, holds the large numbers of original inventions for the NF production process, as for example the Czech Patent 2008-0529 [17]. Not only Elmarco (Czech Republic, www.elmarco.com), as well as Dienes (Germany, www.dienes.net), Freudenberg (Germany, www.freudenberg-filter.com), FibeRio (*U.S.*, www.fiberiotech.com), KATO Tech (Japan, www.keskato.co.jp) and Revolution Fibres (New Zealand, www.revolutionfibres.com) have attained prominences for their sole industrial scale of NF process.

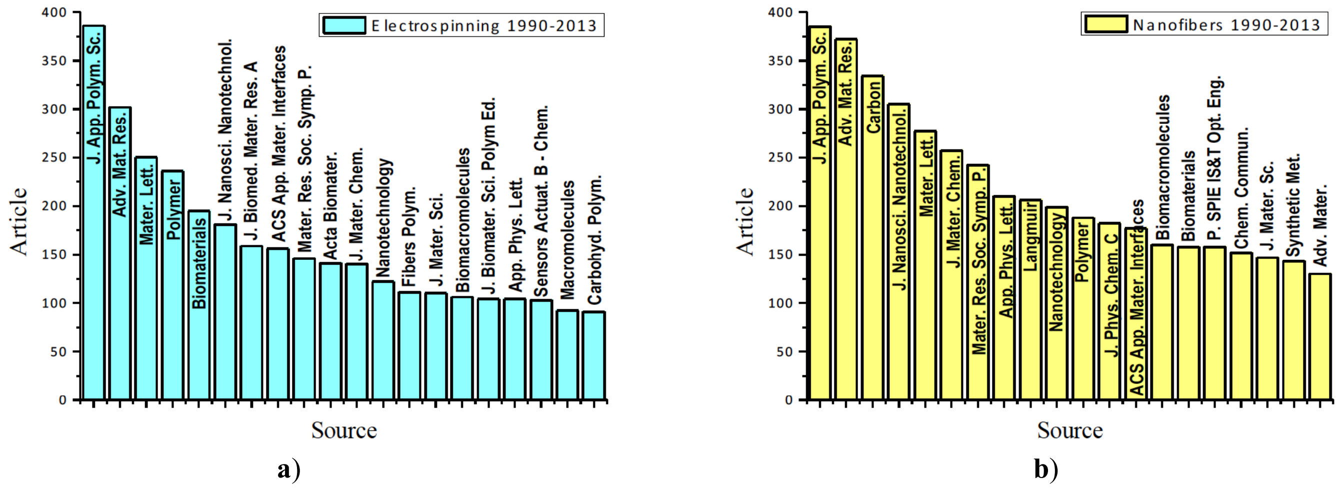


Fig. (5). (**a**) Cumulative number of electrospinning-related publication manuscripts by journals and magazines from 1990 to 2013. *Journal of Applied Polymer Science* leaded this journal ranking by a relative margin. It is important to observe that a number of biomaterial journals follow in the ranking. (**b**) The same research considering nanofibers-related publication manuscripts. Data considering 160 sources worldwide in the period analyzed in both cases from www.scopus.com.

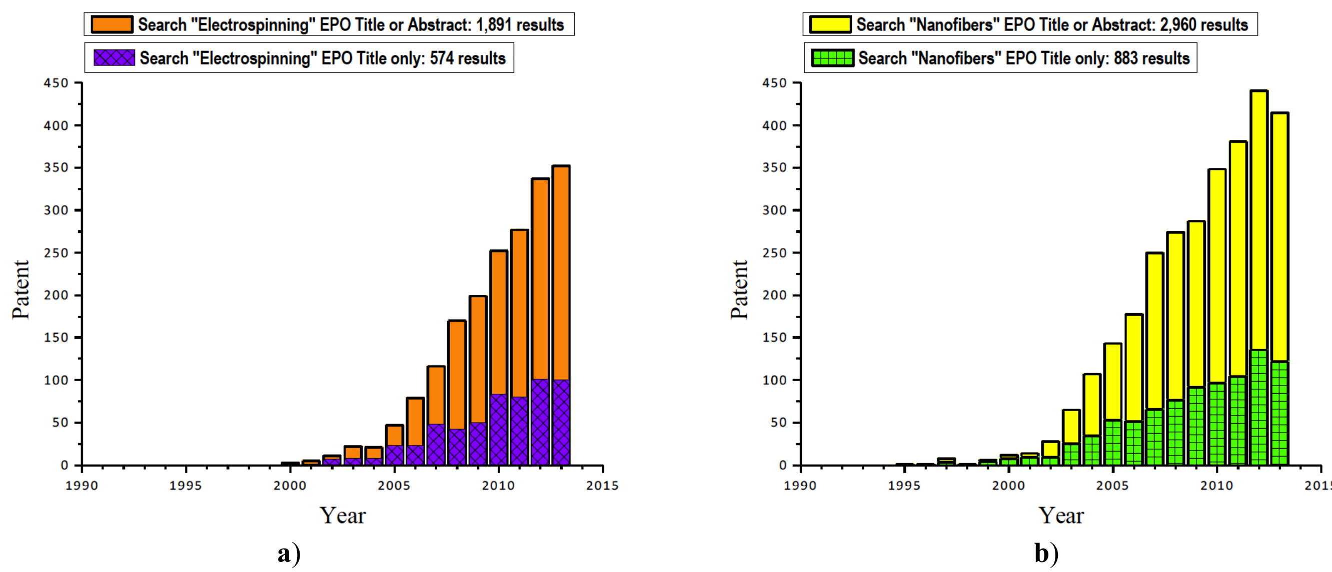
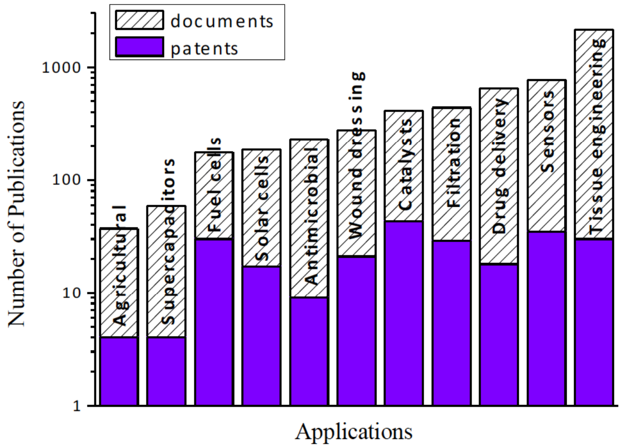


Fig. (6). Frequency distribution results for patent search using (**a**) "electrospinning" in the *title* only and *title or abstract*; (**b**) search using "nanofibers" in the *title* only and *title or abstract*. Data considering year results between 1990 up to 2013 from www.epo.org.

The other class is *product application*. Figuring out how nanofibers substitute / replace, and enhance the performance at particular morphology and process conditions. One example of such patent was issued by Dzenis and Reneker [18] (*U.S.* Patent 6,395,046) who recomended using nanofiber polymers in between laminas of a laminate to enhance delamination resistance. China remains on the top for patent filings in the NF application area, followed by the United States companies. According to Bhardwaj & Kundu [19], over these years, more than 200 natural or synthetic polymer composites have been electropun for a range of applications and the quantity is still rising regularly with time. Some examples of materials used are: polylactic acid, polyurethanes, silk fibroin, collagen / gelatin, casein, chitin, fibrinogen, hyaluronic acid, cellulose and chitosan. It is important to note that this method has been known for over 80 years in the textile industry for manufacturing non-woven fiber fabrics [19].

Fig. (**7 a**) shows that tissue engineering, sensors, drug delivery, filtration and catalysis are the top five researches with most electrospinning applications. It is also possible to see again that the number of scientific papers is much higher than published patents considering the same period. Agriculture and supercapacitors are the new areas to work with this technique, according to (Fig. **7 b**) - they are growing something fast.

In particular, and in recent times, improved worldwide demand in water treatment industrial companies has seen the entry of a quantity of stimulating new players into NF field.



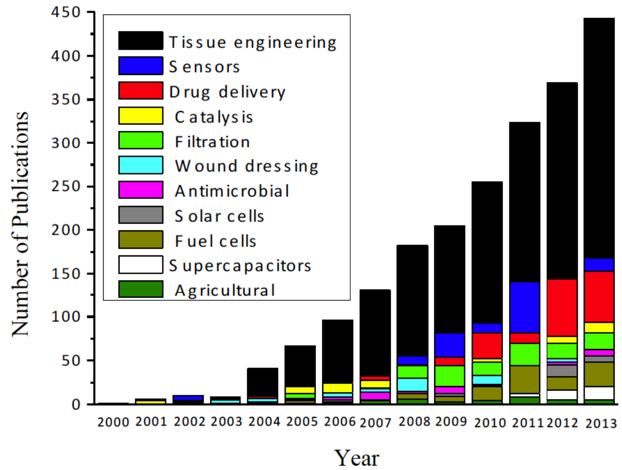


Fig. (7). Number of publications (in log scale) by means of different applications (**a**) in documents or patents; (**b**) Search of the number of publications by year considering most cited applications. For this search were used the terms "electrospinning and application type" at *title* or *abstract*. Data considering year results between 2000 up to 2013 from www.scopus.com.

For reaching energy savings / lower pressure requirements in filtration process, industries continuously recognize and arrange the promising alternatives – include enhancement in filter products. Nanofiber technology set up this shift, opens up novel and broader markets for membrane filtration. It was expected that future filtration market would be around US $700b by the year 2020 [9]. One patent example to cite is related to a procedure for a dust filter bag which develops a profusion of layers comprising a carrier material layer and a nanofiber non-woven tissue layer, proposed by Emig *et al.* [20] (*U.S.* Patent 6,395,046). In this particular case, it is also possible to cite NF companies as Donaldson (*U.S.*, www.donaldson.com), Clarcor (*U.S.*, www.clarcor.com), Ahlstrom (*U.S.*, www.ahlstrom.com), and eSpin (*U.S.*, www.espintechnologies.com), that have already been well known for their nanofibers based quality materials, most of them turned to filtration technology. The fast cognizance between water industrial companies in nanofibers is an unambiguous signal that nanofibers will be perceived as answer for business to succeed and solve some global relevant themes of the present. It is expected that improved number of inventions will happen in liquid membrane domain in the future decade.

Governments have a fundamental role in improving, supporting and providing ways in new inventions, innovations and production of potential commercial patents. Governmental agencies such as the National Natural Science Foundation of China (NSFC), the National Science Foundation (*U.S.*), the National Research Foundation (Singapore), the Deutsche Forschungsgemeinschaft of Germany, the European Union, the Engineering and Physical Sciences Research Council (EPSRC) of the UK for the most expressive countries, as well as CAPES, CNPq and FINEP in Brazil are examples of programs that have supported scientists, industries institutes and other organizations in the development of energy efficient green-technological solutions. NF technology has considerable promises. Additionally, new and performance-enhancing products and processes have been prepared as a result from the steadily growing research communities and funding support.

Thus, the electrospinning and nanofibers portfolios has been considered a promising theme in the literature, due to their importance among industrial researchers, scientists as well as academicians, thus a larger quantity of potential publication manuscripts / patents / products / in NF and ES fields could be expected along the way. For the future improvements in the applicability of these new and tiny fibers, many novel electrospun innovations are being used [19], promoting more potential industrial applications of electrospun products. Some of these inventions comprise coaxial electrospinning [21, 22], modified coaxial electrospinning [23], triaxial electrospinning [24], and side-by-side electrospinning [25], blow assisted electrospinning and others. Further new innovations will also present a variety of properties and advantages, as novel multiple-fluid electrospinning for creating new nanostructures [26] or even continuous filament production [27]. As show in (Fig. **7**), there had been broad attention in using the nanofibrous membranes as tissue engineering scaffolds. A nanoscale fibrous scaffold more closely imitates the extracellular matrix than macroscale scaffolds and supports a 3D surrounding. With nanofibrous scaffolds, cell adhesion, proliferation and differentiation of several types of cells have been observed. Certainly in future electrospun nanofibers will demonstrate to be a potential candidate for a broader variety of applications.

However, the limited number of published manuscripts has yet to reveal several main issues important to nanofibers produced by electrospinning technique. More experiments or even modeling and simulation studies on the fundamental properties of these new materials show great promise in a number of applications.

5. CURRENT AND FUTURE DEVELOPMENT:

To the layman, the production of nanofibers is a new way to produce very tiny fibers. On closer inspection, however, nanofibers produced by electrospinning constitute a fascinating group of materials both from the fundamental and applied standpoints. Electrospinning is a centenary technology that basically consists in an electrostatic fiber manufacture technique that has displayed extra attention and interest in recent years due to its simplicity, versatility and potential for applications in different fields from a large variety of polymer compositions. Another important point is that can be developed for mass production. The notable and cost-effective applications include tissue engineering scaffolds, nanocatalysis, biosensors, wound dressings, filtration, pharmaceutical, optical electronics, healthcare, drug delivery, enzyme immobilization, security and defense, and energy generation and storage. It has in fact four centuries and can be considered among the most ancient materials in human history, but just from 1990s these terms were coined in literature. However, it seems paradoxical that our knowledge of their structure is far from complete, as well as its possible applications in industry (considering the number of patents filled up to now as well as the number of approximately 200 polymers studied).

In this work we presented the last great advances in the electrospinning process since the 1990s. We also discussed one of the most widely methods for manufacturing nanofiber manufacturing and how this method ensured high excellence and high productivity for many industrial sectors. According to the European Patent Office, more than 1,891 patents have been filed around the world in these 25 years that have used the term "*electrospinning*" at title or abstract and 2,960 with the term "nanofibers". These numbers just continue to grow as do total sales worldwide. According to Scopus database, for the same period 11,973 electrospinning document results and 18,679 nanofibers-related were published, and most were manuscripts.

Patents could be considered indicators of successful innovations. The number of nanofibers produced by electrospinning technique patents had been increasing, considering some different databases, due to: *i*) the potential impact of nanofibers; *ii*) the rapid synthesis; *iii*) their recognized relevance in industries. Comparison results from papers and patents are useful because is more plausible that the same filled patents can be reproduced in other languages, more frequent procedure as occurs in manuscripts.

The publication rate has roughly increased exponentially since the beginning of the XXI century. Overall the most significant countries for electrospinning and nanofiber researches were China, *U.S.*, Japan, and South Korea, which indicated high levels of advanced research and development activities.

The recognition of the electrospinning process can be viewed by the fact that over 160 research institutes and universities around the world are studying various aspects of the electrospinning process and the fiber it develops up to now. It was observed recently a rise in academic researches, with the Donghua University (China) and the National University of Singapore as the main university labs and the most productive universities in the almost past quarter century. The number of globally published scientific articles issued worldwide remains higher than the number of patents granted. This result demonstrated the very elevated level of initial activity on scientific technological research. Thus, there are several challenges in the electrospinning process, and a large quantity of basic questions remains open. As a new frontier in nanotechnology, one should agree with Nobel Prize Richard Feynman's famous talk at Caltech in 1959 about a new and promising *era* in science, [28] that "There's Plenty of Room at the Bottom" – certainly considering at least the problem of manipulating and controlling too tiny things as nanofibers.

CONFLICT OF INTEREST

The author(s) confirm that this article content has no conflict of interest.

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